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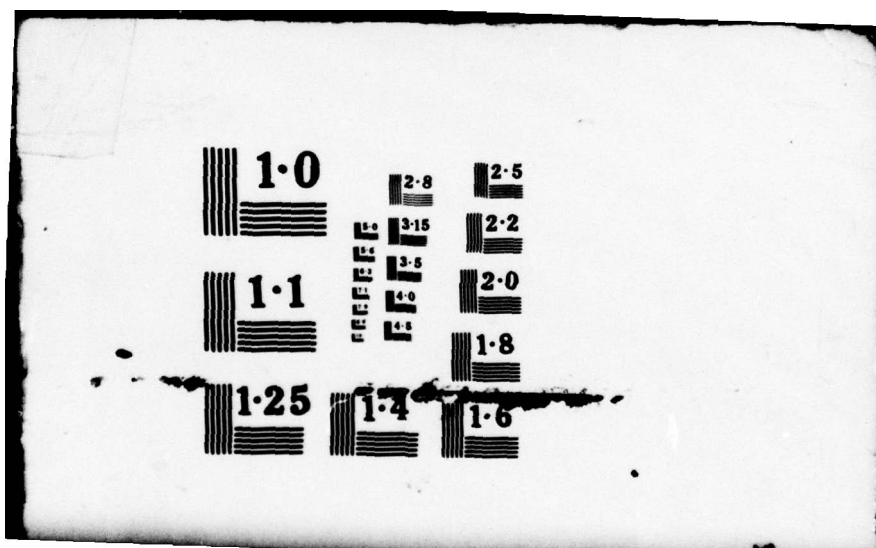
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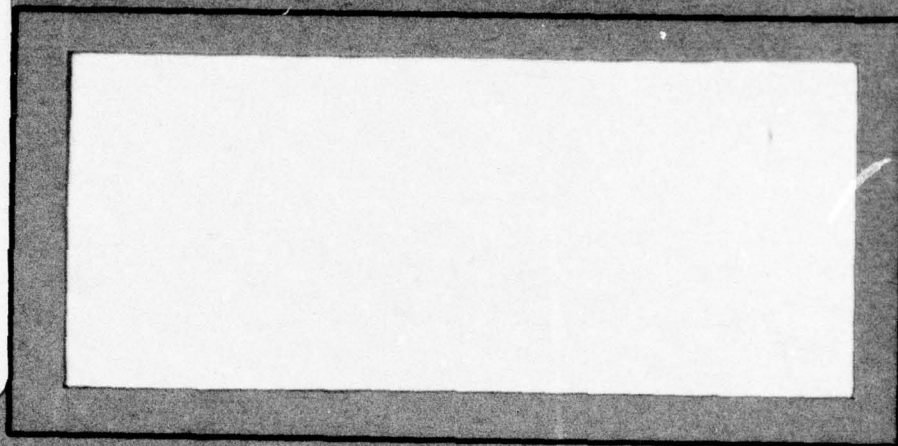


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TUNED DIODE LASER MEASUREMENTS
OF ATMOSPHERIC ABSORPTION PROFILES
IN THE 4.5 μ m TO 5.0 μ m REGION

FINAL REPORT

by
David G. Snyder



Prepared for

U. S. Army Research Office
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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. JOINT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Tuned Diode Laser Measurements of Atmospheric Absorption Profiles in the 4.5 um to 5.0 um Region Micrometers Micrometers		5. TYPE OF REPORT & PERIOD COVERED Technical FINAL: 5/23/76 to 5/23/78
6. AUTHOR(s) David G. Snyder		7. PERFORMING ORG. REPORT NUMBER SAI-78-009-AA1
8. PERFORMING ORGANIZATION NAME AND ADDRESS Science Applications, Inc./ 15 Research Drive Ann Arbor, Michigan 48103		9. CONTRACT OR GRANT NUMBER(s) DAAG29-76-G-0050
10. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office P. O. Box 12211 Research Triangle Park, NC 27709		11. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 11 23 May 78
12. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Final rept. 23 May 76- 23 May 78,		12. REPORT DATE 5/23/78
		13. NUMBER OF PAGES 9 12 18p.
		14. SECURITY CLASS. (of this report) unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited. 1.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Diode laser, absorption, water vapor, carbon dioxide micrometers → This report		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This report is a summary of work funded by the Army Research Office. It describes results obtained from infrared spectra of H ₂ O and CO ₂ in the 4.8 um region taken with a tunable diode laser. For CO ₂ , evidence is given for the inclusion of an additional term in the F-factor over that usually used in the case of the main 4.8 um band. In the case of H ₂ O, strength measurements are compared with the AFGL line parameters, as well as with calculations of Camy-Peyret and Flaud, with the present study supporting the latter. Limited data is also presented on (over) micrometers 390 938		

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investigations of line widths, self-to-foreign broadening coefficients and line shapes for water vapor. In addition to these results, a method is proposed which should enable the measurement of the far wing shape of a line without the need of considering overlap from other lines.

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INTRODUCTION

This is the final report of the A.R.O. sponsored research carried out using the facilities of the U.S.Army's Atmospheric Sciences Laboratory at White Sands Missile Range and conducted by Science Applications, Inc. This study was undertaken to check the accuracy of existing modeling data and to obtain experimental data to improve the modeling data base. The data base generally used for high resolution atmospheric transmission modeling is the AFGL atmospheric absorption line compilation.¹ The quantities of interest for atmospheric modeling being individual line positions, line strengths and pressure broadened line shapes of atmospheric constituents, in this case, water vapor, carbon dioxide and carbon monoxide.

This report is not intended to be a comprehensive technical report, but a brief presentation of the major results with some elaboration on important points being given in tables and figures. A more extensive ECOM technical report covering this research is in preparation.

EXPERIMENTAL SETUP

The main experimental equipment used in this study is shown schematically in Figure 1. The infrared radiation was supplied by a tuned diode laser system manufactured by A. D. Little, which consists of a diode laser, helium dewar, chopper, mode separating monochrometer and tuning rate germanium etalon. The absorption cells shown in Figure 1 consisted of a 20 cm long, straight through cell which was filled with a calibration gas as well as a 60 cm straight through cell and a two meter multiple path White cell; either of which could be filled with the gas of interest. The White cell with a base length of 2 meters was capable of supplying optical path

lengths up to 120 meters, while the 20 cm calibration gas cell was mounted on a precision translator so that it could be moved in and out of the IR beam.

The infrared radiation was detected by a Judson InSb photovoltaic detector, with output from the detector being sent to a P.A.R. model 128 lock-in amplifier. The amplifier output was then displayed on the Y axis of an X-Y recorder while the X axis was driven linearly with the diode current. An alternate way of recording the data (which was developed late in the research program) was through the use of a Hewlett Packard 2100A minicomputer. In using the computer for data acquisition, signals from the lock-in amplifier were sent directly to an analog to digital converter in the computer while a separate oscillator was used to trigger the A-to-D at regular intervals. Initiation of the digitization process was accomplished by monitoring the diode current on a second A-to-D channel and starting the acquisition of a specified number of data points when the change in this current exceeded a given threshold. Once implemented, this data acquisition system allowed for more sophisticated data reduction procedures than could be accomplished with the analog data.

MEASUREMENT TECHNIQUES

The frequency of an absorption line of interest was determined by placing the calibration cell in the beam and comparing the unknown line positions with those of the calibration gas. By placing the germanium etalon in the beam during a subsequent scan, the frequency difference of the lines could be determined using the etalon fringes, which had a nominal spacing of 0.0495 cm^{-1} . Generally carbon monoxide was used as a calibration gas and the frequencies of the CO lines were taken from Todd et. al.²

Both line strengths and line positions were measured using a low pressure gas fill (on the order of a few Torr or less) so that the line profiles

would be nearly Doppler. The line strengths were then evaluated using the observed peak line absorption and the calculated Doppler width while a small correction was applied to this value to account for the minimal pressure broadening present. For cases where pressure broadening itself was being investigated, the line widths were determined in a straight-forward manner using the etalon fringes.

EXPERIMENTAL RESULTS

Carbon Dioxide

Line positions for carbon dioxide were measured throughout the 5.0 μm region using the procedures discussed above. In particular, the position of the Q-branch lines of the two primary hot bands in this region, namely the $(20^00 + 01^10)_I$ and the $(12^20 + 01^10)_I$, were used to evaluate molecular parameters for CO_2 . In general, these parameters showed only slight discrepancies compared with those tabulated for the AFGL compilation.¹

An outstanding feature of the CO_2 bands in this region, the $(11^10 + 00^00)_I$ band and its hot bands, is that the strengths of their lines are strongly influenced by coriolis interactions. This effect is usually taken into account by multiplying the rigid rotor strength term by a so called F-factor. For these CO_2 bands the form of this F-factor is usually assumed to be $(1 + \zeta m)^2$, where ζ is the coriolis interaction constant and m is an indexing number equal to $-J$ for the P branch and $J + 1$ for the R branch (the Q branch strengths being unaffected). This form of the F-factor arises from 2nd order perturbation theory, the lowest order in which this effect will appear. However, the present study has found experimental evidence indicating that for the $(11^10 + 00^00)_I$ band, one must include a higher order term leading to an F-factor of the form $(1 + \zeta_1 m + \zeta_2 m^2)^2$. This is shown in Figure 2, which is a plot of square root of the F-factor

vs. the indexing number m . The plotted points are experimentally derived and the error bars indicate $\pm 10\%$ uncertainty, corresponding to roughly a $\pm 20\%$ uncertainty in the strength measurement. As indicated in this plot, a linear fit cannot adequately fit these points, even with the over generous error estimates, while a quadratic fit does very well. Additional data, especially measurements of P branch lines, would be valuable to adequately substantiate this result. In contrast to this band, the measured strengths of four P branch lines and the Q branch in the $(20^00 + 01^10)_1$ band fit the original form of the F-factor quite well without using a quadratic term.

Water Vapor

The strongest water vapor lines in this region are due to the bending fundamental ν_2 . One of the purposes of this study was to check the accuracy of the AFGL¹ line compilation and to supplement it where required. However, early in the course of this study Camy-Peyret and Flaud³ published calculations of positions and strengths for the lines of the ν_2 band, based on very high resolution Fourier transform spectra. Therefore, comparisons of the results of the present study have been made with this data as well as with the AFGL tabulation.

As shown in Table 1, line strengths were measured for thirteen lines in the ν_2 band while the positions of five of these could be accurately determined relative to the calibration gas. The comparisons of this table indicate that the line positions agree with the results of Camy-Peyret and Flaud to within 0.003 cm^{-1} for all lines, while disagreement is found with the AFGL values by 0.035 cm^{-1} in one case and 0.01 cm^{-1} in two others. In comparing the line strengths, the present data shows substantially better agreement with Camy-Peyret and Flaud than with the AFGL compilation, but in several cases discrepancies are still significant. In general,

however, it appears that the Camy-Peyret and Flaud values for both line strengths and positions are to be preferred.

Strengths have also been measured for several lines in the ν_1 - ν_2 and ν_3 - ν_2 hot bands which have also been studied by Flaud et. al. Unfortunately, the present measurements do not seem to agree well with either their study or with AFGL. However, observed discrepancies may be due simply to line misidentification, as none of the positions of these lines could be accurately determined relative to the CO calibration lines. More data needs to be taken in these bands since, as Camy-Peyret and Flaud have indicated⁴, the ν_1 - ν_2 line strengths are of particular importance for adequate understanding and modeling of the water molecule.

Although the majority of this study was devoted to evaluation of line positions and strengths, measurements were also begun to investigate line shapes and foreign (N_2) broadening coefficients for water vapor lines. To do this, three absorption lines were chosen with a wide range of line strengths and the limited data collected on these lines are given in Table 2.

Because of the difficulties involved in measuring individual line widths to a high degree of accuracy, a new method has been developed to evaluate the self-to-foreign broadening ratio. This method consists of generating the absorption profile of a given water vapor line using a path length l and pure water vapor pressure P , yielding an optical depth $P l$. Subsequent scans are then taken using a water vapor pressure decreased by some factor n and a path length increased by the same factor so that the optical path depth is identical to that of the first scan ($P/n \cdot n l = P l$). The profiles observed under these new conditions are then compared to the initial water vapor profile and nitrogen is added until the peak absorption is the same in the two cases. If it is assumed that the line shape for

self and foreign broadening is the same, then under those conditions for which the peaks are equal, the half-widths are also equal and the self-to-foreign broadening ratio is given directly by:

$$\frac{PN_2}{P-P/n}$$

where PN_2 is the partial pressure of the nitrogen added. This is true because the PN_2 Torr of nitrogen added in the second case broadens the same as the $(P-P/n)$ Torr of water removed in going from the first case to the second.

Although, at this time, only limited data was collected on the self-to-foreign ratios for water vapor, the values for the lines at 2097 and 2107 cm^{-1} of Table 2 agree reasonably well with the average value of 5.0 accepted for this molecule. However, the self-broadened width for the 2136 cm^{-1} line is larger than that predicted from Anderson theory^{5,6} by approximately a factor of two, while the foreign broadened width for the line at 2107 cm^{-1} is larger by approximately 32%.

Since the AFGL tabulation depends heavily on Anderson theory predictions, additional data should be gathered on self-broadened widths as well as on self-to-foreign broadening ratios (using the procedures outlined above) to determine the origin of these discrepancies. Since quantum many-body calculations of half-widths⁷ disagree with Anderson predictions, especially for higher rotational states where both theories depend heavily on the choice of the minimum collision diameter, these measurements would also be valuable in resolving these basic questions.

The self-broadened data for the lines at 2107 cm^{-1} and 2136 cm^{-1} , as well as self and foreign broadened data for a line at 2023 cm^{-1} , were also used to determine if there is any justification for the use of a non-voigt

shape for water vapor. To do this, the observed profiles were compared with the standard Voigt shape and with a "super-Voigt" shape based on the "super-Lorentz" profile of Trusty et. al. For the 2107 cm^{-1} line these comparisons did not yield definitive results because, with the large half-width of this line, the profile observable with the diode system did not extend far enough into the line wings for the two profiles to be significantly different. For the self-broadened data of the 2136 cm^{-1} line, however, the observed profile showed substantially better agreement with the Voigt shape than with the "super-Voigt". Unfortunately, this line is sufficiently strong so that residual H_2O absorption in the air path between the diode system and the absorption cell had to be corrected for introducing possible errors. The data gathered on the 2023 cm^{-1} line, although not completely analyzed at this time, does qualitatively indicate that the nitrogen broadened profile falls off less rapidly in the wings than the self-broadened profile. This suggests the possibility of "super-Voigt" behavior in the presence of foreign broadening even though this is not indicated for self-broadening.

In experimentally measuring the absorption of spectral line wings, one encounters severe difficulties. These arise because the Lorentz shape falls off increasingly slowly as one gets more than a few half widths from line center. This slow fall-off coupled with the decreasing absorption as one goes into the wings, makes accurate measurement of the absorption level extremely difficult. In addition, as one gets farther from the line center, the absorption due to the line of interest will no longer be large enough for one to neglect the contributions from wings of adjacent lines. If one is to account for these other lines, one must have accurate data on their positions, strengths and widths, and must be able to make valid

assumptions regarding their shapes. Consequently, the problem of accurately determining the line shape becomes almost impossible unless one can eliminate the interference due to this line overlap. In the present study, a method has been devised which shows good promise of allowing one to study far wing shapes by eliminating this overlap problem. This method involves observing a line at fairly low pressure so that the pressure broadening is small. Although under these conditions the line center will have a nearly Doppler profile, the wings will still be mainly the result of the pressure broadening. If one can observe a strong line with a sufficiently large path length, then the wings will be observable out to many times the pressure broadened width while still being close enough to line center so that other lines may be neglected.

Some features of this method are illustrated in Figure 3. While this spectrum was taken for the purpose of studying the water vapor absorption line on the right, the strong carbon monoxide absorption line, P(9), on the left illustrates the method. The upper trace was taken with the carbon monoxide cell removed from the optical path and the small carbon monoxide absorption is due to contamination in the nitrogen gas used to buffer the water vapor. The lower trace has the 20 cm long cell 10 Torr of carbon monoxide placed in the beam. The CO line in this scan is listed in the AFGL compilation as having a foreign broadening coefficient of $0.0648 \text{ cm}^{-1} \text{ atm}^{-1}$. Assuming a self-to-foreign ratio of 1.1, the broadened half-width of this line is only 0.000938 cm^{-1} . Absorption of at least a few percent is evident at about 0.1 cm^{-1} from line center (about two fringe spacings). In general, CO lines are spaced about 4 cm^{-1} apart, or for the above case, 4000 half-widths. Under these conditions, measurements even 100 half-widths from line center are essentially unaffected by the wings of adjacent lines.

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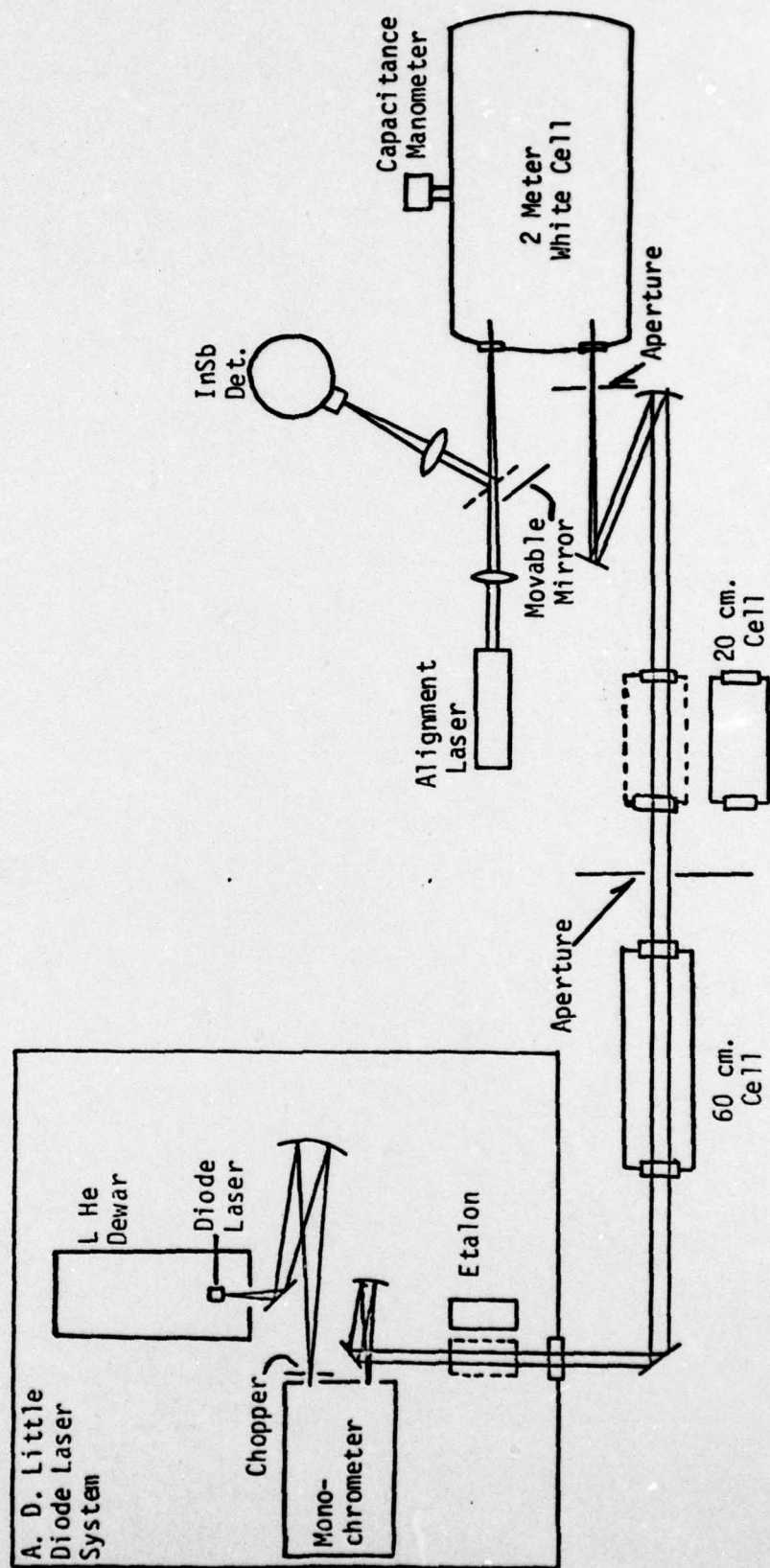


Figure 1. Schematic of Experimental System

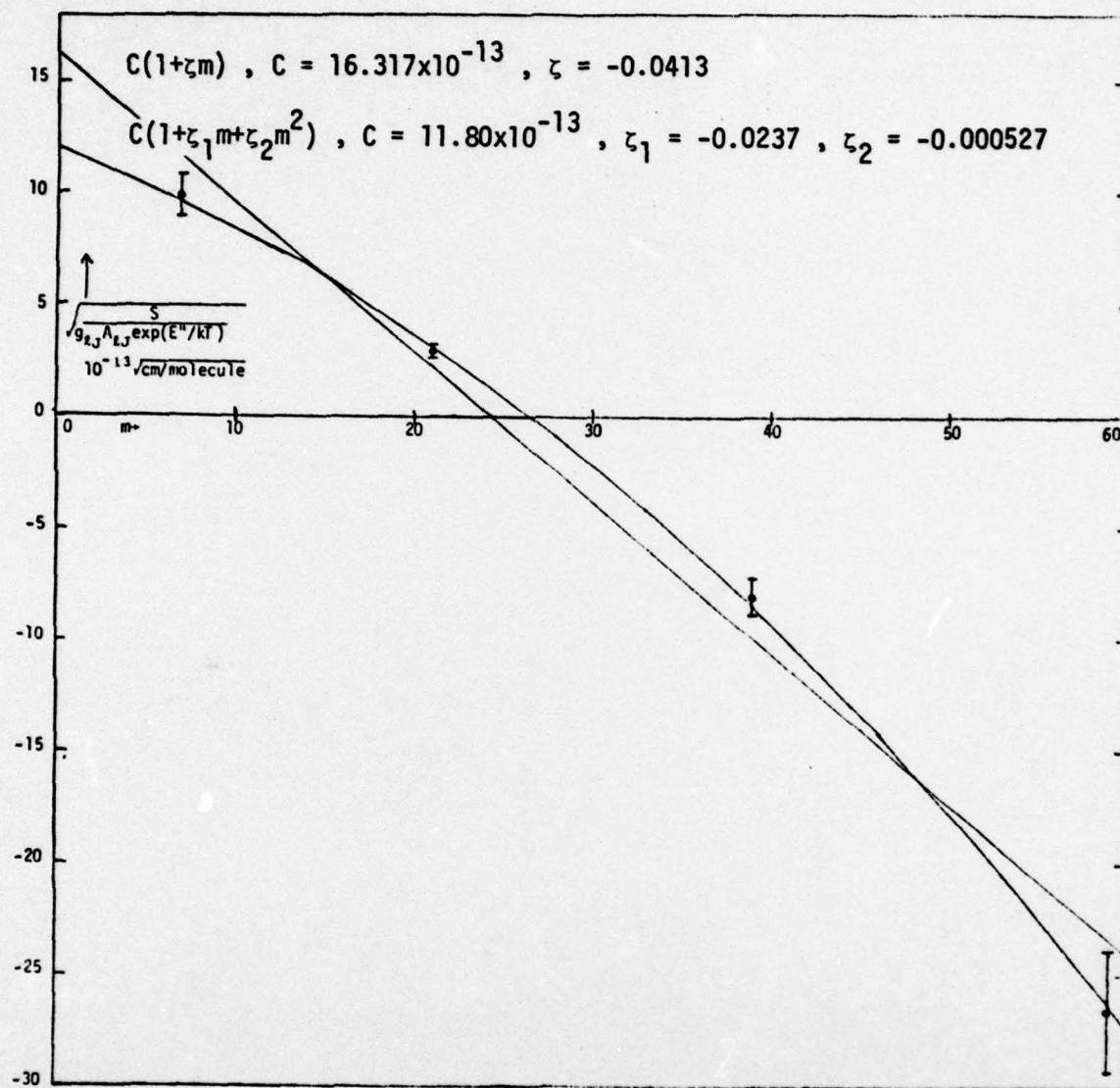


Figure 2. Carbon Dioxide F-Factor for the $(11^1_0 + 00^0_0)_1$ Band.

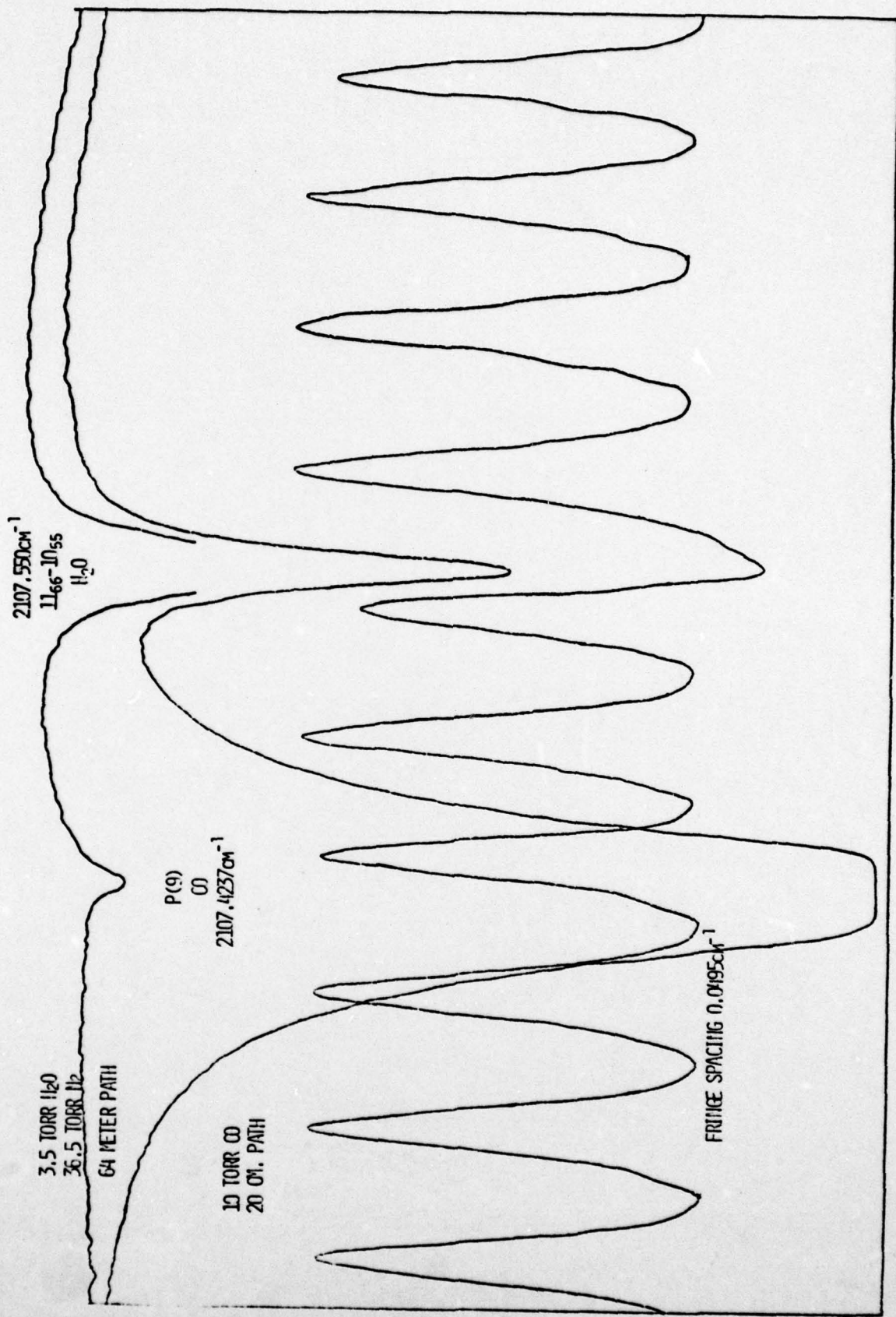


Figure 3. Tuned Diode Laser Spectrum.

Table 1. Water Vapor Line Positions and Strengths.

	POSITION (cm ⁻¹)			STRENGTH (cm/molecule)		
	This Work	Ref. 3	AFGL	This Work	Ref. 3	AFGL
ν_2						
10 ₃₇ ⁺⁹²⁸	2081.874	2081.874	2081.910	—	4.57×10 ⁻²³	3.52×10 ⁻²³
10 ₆₅ ⁺⁹⁵⁴	—	2087.408	2087.400	1.77×10 ⁻²²	2.05×10 ⁻²²	1.78×10 ⁻²²
10 ₆₄ ⁺⁹⁵⁵	—	2090.023	2089.920	7.34×10 ⁻²³	6.76×10 ⁻²³	5.45×10 ⁻²³
9 ₃₇ ⁺⁸⁰⁸	—	2097.368	2097.370	4.79×10 ⁻²³	4.78×10 ⁻²³	4.88×10 ⁻²³
6 ₅₂ ⁺⁵²³	2106.345	2106.347	2106.350	2.41×10 ⁻²³	2.10×10 ⁻²³	3.64×10 ⁻²³
5 ₅₀ ⁺⁴²³	—	2105.781	2105.800	6.34×10 ⁻²⁴	6.01×10 ⁻²⁴	1.06×10 ⁻²³
11 ₆₆ ⁺¹⁰⁵⁵	2107.550	2107.547	2107.510	1.87×10 ⁻²³	2.10×10 ⁻²³	1.61×10 ⁻²³
11 ₆₅ ⁺¹⁰⁵⁶	—	2114.427	2114.430	5.03×10 ⁻²³	6.14×10 ⁻²³	4.43×10 ⁻²³
9 ₇₃ ⁺⁸⁶²	—	2114.980	2114.980	7.31×10 ⁻²³	7.81×10 ⁻²³	6.11×10 ⁻²³
9 ₇₂ ⁺⁸⁶³	—	2115.018	2115.010	2.14×10 ⁻²²	2.34×10 ⁻²²	1.83×10 ⁻²²
12 ₅₇ ⁺¹¹⁴⁸	—	2116.225	2116.240	6.06×10 ⁻²⁴	7.72×10 ⁻²⁴	2.09×10 ⁻²⁴
7 ₅₃ ⁺⁶²⁴	2121.271	2121.269	2121.280	1.13×10 ⁻²³	1.10×10 ⁻²³	1.89×10 ⁻²³
12 ₆₇ ⁺¹¹⁵⁶	2124.290	2124.291	2124.290	1.28×10 ⁻²³	1.75×10 ⁻²³	1.58×10 ⁻²³
8 ₈₁ ⁺⁷⁷⁰	—	2136.144	2136.140	2.18×10 ⁻²²	2.77×10 ⁻²²	1.81×10 ⁻²²
8 ₈₀ ⁺⁷⁷¹	—	—	—	—	—	—

Table 2. Measured H₂O Line Parameters.

$\bar{\nu}(\text{cm}^{-1})$	ID	MEASURED PARAMETERS				AFGL	
		$\gamma_s (\text{cm}^{-1} \text{ atm}^{-1})$	γ_s / γ_{N_2}	$\gamma_{N_2} (\text{cm}^{-1} \text{ atm}^{-1})$	$S \left(\frac{\text{cm}^{-1}}{\text{molec} \cdot \text{cm}^{-2}} \right)$	$\gamma_{\text{air}} (\text{cm}^{-1} \text{ atm}^{-1})$	$S \left(\frac{\text{cm}^{-1}}{\text{molec} \cdot \text{cm}^{-2}} \right)$
2107.510	11 ₆₆ - 10 ₅₅	.390	4.78	.0816	2.20 x 10 ⁻²³	.0604	1.610 x 10 ⁻²³
2097.370	9 ₃₇ - 8 ₀₈		5.25		4.82 x 10 ⁻²³	.0559	4.880 x 10 ⁻²³
2136.140	8 ₈₁ - 7 ₇₀	.223				{ .0356	1.360 x 10 ⁻²²
2136.140	8 ₈₀ - 7 ₇₁						
						.0356	.451 x 10 ⁻²²